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External electric field effects on absorption and fluorescence of anthracene–$(CH_2)_n$–naphthalene bichromophoric molecules doped in a polymer film

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Abstract

Methylene-linked bichromophoric molecules of naphthalene and anthracene, i.e., 9-anthryl–$(CH_2)_n$–1-naphthyl exhibit a very efficient photoexcitation energy transfer (EET) from the naphthalene to anthracene moieties in a polymer film, resulting in the observation of only the anthracene-like fluorescence even for excitation of the naphthalene moiety. Electrofluorescence spectra of the linked compounds are very different from those of a mixture of naphthalene and anthracene, indicating that methylene chain plays a significant role in excitation dynamics and its electric field effect. At high concentrations, where both monomer fluorescence and excimer fluorescence of anthracene are observed, the excimer fluorescence of the linked compounds is enhanced by an electric field, whereas the monomer fluorescence is quenched by an electric filed, suggesting that the intermolecular excimer formation is remarkably enhanced by an electric field in the linked compounds.

Keywords: Energy transfer; Electric field effects; Excimer formation; Electroabsorption spectrum; Electrofluorescence spectrum; Linked compound

1. Introduction

The effects of electrostatic fields on photochemical reactions, such as photoinduced electron transfer, photoisomerization, and excimer formation, have been extensively studied as a subject of great importance in chemical physics. Measurements of solvent polarity dependence of optical spectra are generally used to obtain information on field effects on photochemical behavior in the system concerned [1,2]. This method is useful; however, microscopic solute–solvent interactions as well as dependencies of the reaction on other solvent parameters often interfere with the detailed analysis of the mechanism. External electric field effects on photochemical reactions in a solid phase have been widely investigated in recent years [3,4]. Since the external electric field can be regarded as the single perturbation to be considered in such a case, measurements of the external electric field effects in a solid are expected to provide unique information on photochemical processes.

In a solid film, the rate of photoinduced electron transfer has been shown to be markedly influenced by an external electric field in mixtures of donor and acceptor molecules and methylene-linked compounds of donor and acceptor [4–8]. The field dependencies of the electron transfer of a linked compound and of a corresponding mixture are different from each other. For the electron transfer between *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) doped in a film, the marked difference in the electric field effect has been observed between the mixture and the linked compound [5–7]. Following excitation of ECZ, the monomer fluorescence of ECZ is reduced by an electric field in a mixture of ECZ and DMTP. In the linked compound with a short methylene chain, on the other hand, the monomer fluorescence is enhanced by an electric field at a low dopant concentration, which can be ascribed to the field-induced increase in rate of back-electron transfer through a methylene chain following photoinduced electron transfer from ECZ to DMTP.

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In the present paper, we report the electric-field-induced change in fluorescence spectra as well as in absorption spectra of methylene-linked anthracene and naphthalene, i.e., 9-anthryl–$(CH_2)_n$–1-naphthyl with $n = 1, 3$, and 6, and of a mixture of anthracene and naphthalene doped in a poly(methyl methacrylate) (PMMA) film. Hereafter, 9-anthryl–$(CH_2)_n$–1-naphthyl is denoted by A(*n*)N. The photoexcitation dynamics of A(*n*)N has been extensively studied as a model of intramolecular photoexcitation energy transfer (EET) process [9–14]. A(*n*)N exhibits an efficient EET process from the naphthalene to anthracene moieties, the yield of which depends on the length of the methylene chain. The electric field effects on fluorescence observed in A(*n*)N are found to be markedly different from the ones in the mixture, indicating that the methylene chain plays a significant role in photoexcitation dynamics and in its electric field dependence.

2. Experimental

The A(*n*)N compounds were synthesized according to the literature procedure [15]. Naphthalene and anthracene were purchased from Tokyo Kasei Co. and purified by a vacuum sublimation. PMMA (MW = 120,000, Aldrich) was purified several times by a precipitation with a mixture of benzene and methanol and by an extraction with hot methanol. A certain amount of benzene solution of PMMA containing solute molecules was cast on an ITO-coated quartz substrate by a spin coating method, and the polymer film was evaporated to eliminate benzene. Then a semitransparent aluminum film was deposited on the dried polymer film. The ITO and aluminum films were used as electrodes. The thickness of the polymer film was determined using a Nanospec/AFT system (Nanometrics, M3000). The concentration of the sample was in the range of 0.1–10 mol% in its ratio to the monomer unit of PMMA.

All measurements were performed at room temperature under vacuum conditions. Plots of the electric-field-induced change in absorption intensity or fluorescence intensity as a function of wavelength, which are denoted by electroabsorption spectrum and electrofluorescence spectrum, respectively, were measured using electric field modulation spectroscopy with the same apparatus as reported previously [5–8]. A sinusoidal ac voltage with a modulation frequency of 40 Hz was applied between the electrodes, and the value of the field-induced change in absorption intensity or fluorescence intensity was detected with a lock-in amplifier at the second harmonic of the modulation frequency. A dc component of the transmitted light intensity or the emission intensity was also observed. Applied field strength was evaluated from the applied voltage divided by the polymer thickness. Hereafter, electroabsorption and electrofluorescence spectra are abbreviated as E–A and E–F spectra, respectively. Applied field is denoted by $\boldsymbol{F}$ and its strength is represented by rms.

3. Results and discussion

When an electric field is applied to molecules, each energy level is shifted, which is known as the so-called Stark shift. The magnitude of the level shift depends on the electric dipole moment ($\boldsymbol{\mu}$) and the molecular polarizability ($\boldsymbol{\alpha}$) of the state concerned. When the magnitude of $\boldsymbol{\mu}$ or $\boldsymbol{\alpha}$ in the excited state is different from the one in the ground state, the absorption spectra as well as the emission spectra are shifted since the magnitudes of the level shift in both states are different from each other. For an isotropic and immobilized sample such as a polymer film where sample molecules are randomly distributed, the presence of $\boldsymbol{F}$ will broaden an isolated transition due to the change in electric dipole moment following absorption transition, giving rise to the E–A spectrum, the shape of which is the second derivative of the absorption spectrum. If the magnitude of the change in molecular polarizability is significant, the shape of the E–A spectrum is the first derivative of the absorption spectrum. If the transition moment is affected by $\boldsymbol{F}$, the shape of the E–A spectrum is the same as that of the absorption spectrum. Thus, by assuming that the isotropic distribution remains unchanged in the presence of $\boldsymbol{F}$, the E–A spectrum ($\Delta A(\nu)$) for a random distribution system is expected to be given by a linear combination of the absorption spectrum, its first and second derivative spectra as follows [3,4,16]:

$$\Delta A(\nu) = (f\boldsymbol{F})^2 \left[A' A(\nu) + B' \nu \frac{\mathrm{d}\{A(\nu)/\nu\}}{\mathrm{d}\nu} + C' \nu \frac{\mathrm{d}^2\{A(\nu)/\nu\}}{\mathrm{d}\nu^2} \right] \tag{1}$$

$$B' = \frac{\Delta\bar{\alpha}/2 + (\Delta\alpha_m - \Delta\bar{\alpha})(3\cos^2\chi - 1)/10}{hc} \tag{2}$$

$$C' = |\Delta\boldsymbol{\mu}|^2 \frac{[5 + (3\cos^2\xi - 1)(3\cos^2\chi - 1)]}{30h^2c^2} \tag{3}$$

where $\Delta\boldsymbol{\mu}$ and $\Delta\boldsymbol{\alpha}$ are the differences in electric dipole moment and molecular polarizability, respectively, between the ground state (g) and the excited state (e), i.e., $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_e - \boldsymbol{\mu}_g$ and $\Delta\boldsymbol{\alpha} = \boldsymbol{\alpha}_e - \boldsymbol{\alpha}_g$. $\Delta\bar{\alpha}$ denotes the trace of $\Delta\boldsymbol{\alpha}$, i.e., $\Delta\bar{\alpha} = (1/3)\mathrm{Tr}(\Delta\boldsymbol{\alpha})$. $\Delta\alpha_m$ is the diagonal component of $\Delta\boldsymbol{\alpha}$ with respect to the direction of the transition dipole moment; χ is the angle between the direction of $\boldsymbol{F}$ and the electric vector of the light; ξ is the angle between the direction of $\Delta\boldsymbol{\mu}$ and the transition dipole moment; and f is the internal field factor.

Fig. 1 shows the E–A spectra of A(1)N, A(3)N, and A(6)N doped in a PMMA film at 1.0 mol%, together with the corresponding absorption spectra. The absorption spectra of A(*n*)N can be described as a superposition of respective absorption spectra of anthracene and naphthalene [12–14]. The structured absorption band in the region of 330–400 nm is assigned to the S_1 (^1L_a) ← S_0 transition of the anthracene moiety. The position of the 0–0 transition to the S_1 state remains unchanged with a change in the number of the methylene unit. The naphthalene moiety shows the two absorption bands: the S_1 (^1L_b) ← S_0 transition in the region of 310–320 nm and the S_2 (^1L_a) ← S_0 transition in the region of 270–300 nm. The very strong absorption at wavelengths less than 270 nm is assigned to the S_3 (^1B_b) ← S_0 transition of the anthracene moiety.

All the observed E–A spectra in the 330–400 nm region are very similar in shape to the first derivative of the corresponding absorption spectrum, indicating that the field-induced change

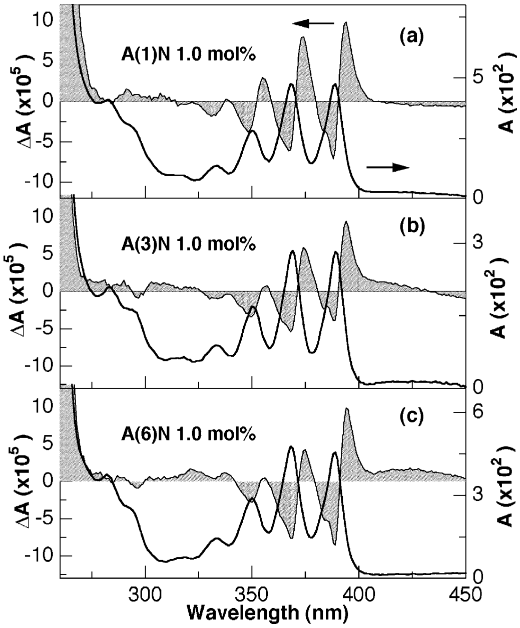

Fig. 1. E–A spectra (shaded line) and absorption spectra (solid line) of A(1)N (a), A(3)N (b), and A(6)N (c) doped in a PMMA film at 1.0 mol%. Applied field strength was 1.0 MV cm^{-1}.

in absorption intensity in this region comes from the change in molecular polarizability following excitation into the S_1 state of the anthracene chromophore. Actually, the E–A spectra of the $S_1 \leftarrow S_0$ absorption band of the anthracene moiety are well fitted by the first derivative, and the $\Delta\bar{\alpha}$ values are evaluated to be 47 ± 9 in units of Å^3 for A(1)N, A(3)N, and A(6)N, by using Eqs. (1) and (2). Here, it is assumed that the molecular polarizability is isotropic, i.e., $\Delta\alpha_m = \Delta\bar{\alpha}$, and the local field is the same as the applied field, i.e., $f = 1$ in Eq. (1). The zeroth derivative component of the $S_1 \leftarrow S_0$ absorption spectrum is negligibly small in all the E–A spectra of A(n)N, indicating that the transition dipole moment to the S_1 state of the anthracene moiety is not influenced by $\boldsymbol{F}$. The $S_3 \leftarrow S_0$ transition of the anthracene moiety also shows a strong electric field effect, but the absorption bands of the naphthalene moiety are affected by $\boldsymbol{F}$ much less than those of the anthracene moiety.

The E–A spectra of anthracene doped in a PMMA film at 1.0 and at 5.0 mol% are shown in Fig. 2a and b, respectively, together with the absorption spectra. The E–A spectra of anthracene exhibit the shape very similar to the first derivative of the absorption spectrum, as in the case of A(n)N. The $\Delta\bar{\alpha}$ value of anthracene is thus evaluated to be about 50 Å^3 by assuming that the molecular polarizability is isotropic and that the local field is the same as the applied field. Fig. 2c shows the E–A and absorption spectra of a mixture of anthracene and naphthalene separately doped in a PMMA film. It is clearly seen that the addition of naphthalene hardly affects the E–A and absorption spectra of the $S_1 \leftarrow S_0$ absorption band of anthracene; both absorption spectrum and E–A spectrum of a mixture of anthracene (5 mol%) and naphthalene (5 mol%) are essentially the same in shape as those of anthracene alone. Fig. 2d shows the E–A spectrum of naphthalene doped in a PMMA film, together with the absorption spectrum. The shape of the E–A spectrum

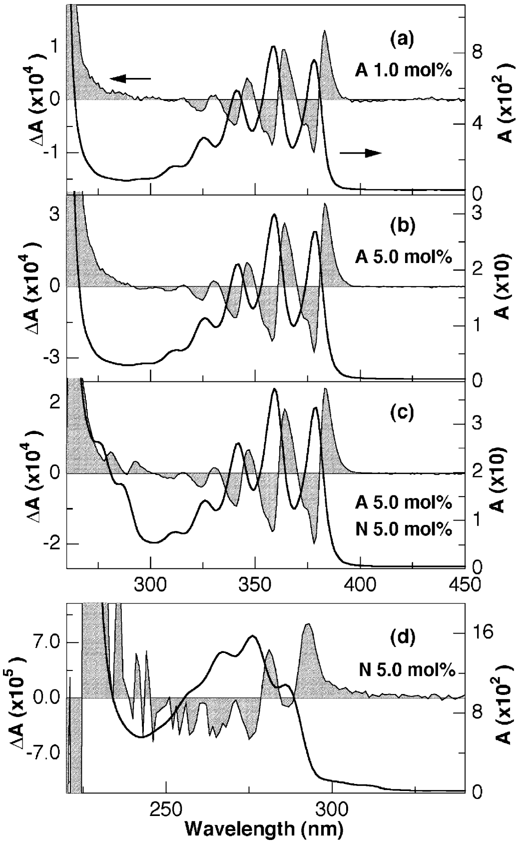

Fig. 2. E–A spectra (shaded line) and absorption spectra (solid line) of anthracene (1.0 mol%) (a), anthracene (5.0 mol%) (b), a mixture of anthracene (5.0 mol%) and naphthalene (5.0 mol%) (c), and naphthalene (5.0 mol%) (d) doped in a PMMA film. Applied field strength was 0.7 MV cm^{-1}.

of naphthalene is also the same as that of the first derivative of the absorption spectrum. The value of $\Delta\bar{\alpha}$ upon excitation to the S_2 state of naphthalene is evaluated to be about 50 Å^3 using the same assumptions as those used for anthracene.

Fig. 3 shows the E–F spectra of A(1)N, A(3)N, and A(6)N doped in a PMMA film at 1.0 and 5.0 mol%, respectively, together with the corresponding fluorescence spectra. Excitation was done at the wavelengths where only the naphthalene moiety is excited and the field-induced change in absorption intensity is very small. Irrespective of the excitation wavelength, only the fluorescence from the anthracene moiety is observed in all the linked compounds, indicating that the very efficient intramolecular EET process occurs from the naphthalene to anthracene moieties even in a PMMA film. At a low concentration of 1.0 mol%, the fluorescence spectra of A(n)N exhibit the well-defined vibronic structure of the $S_1 \rightarrow S_0$ fluorescence of anthracene, and their field-induced changes are similar in shape to the first derivative of the corresponding fluorescence spectrum. This result is consistent with the fact that the first derivative is dominant in the E–A spectra; both the E–A and E–F spectra monitor the difference in electronic property between the S_0 and S_1 states of the anthracene chromophore. The field-induced change in total fluorescence intensity is negligibly small in all the E–F spectra of the linked compounds. As mentioned above, the transition moment to the S_1 state is not affected by

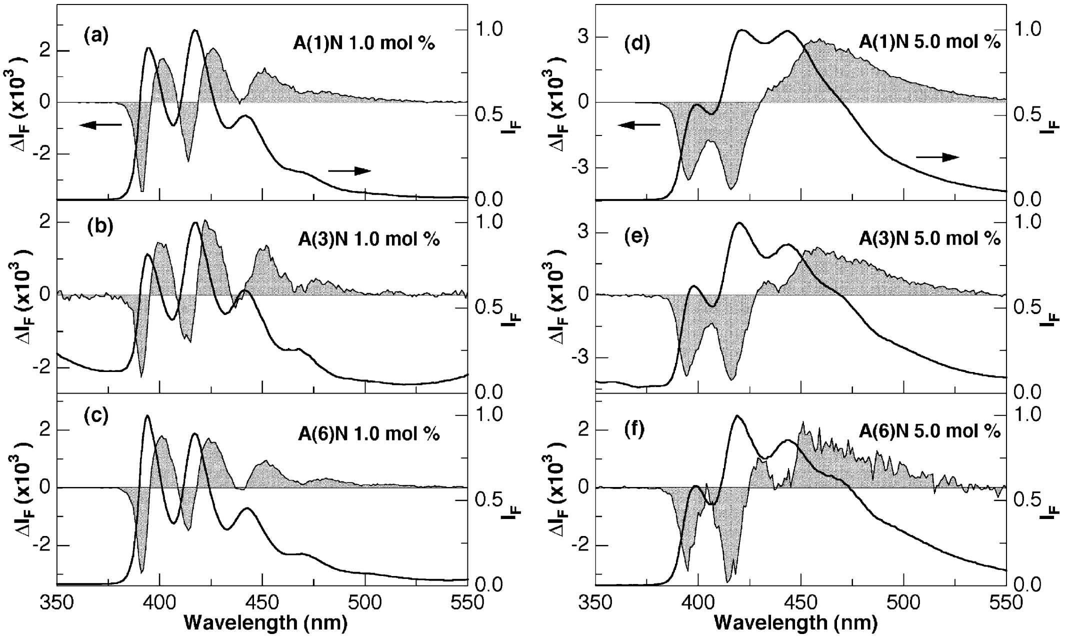

Fig. 3. E–F spectra (shaded line) and fluorescence spectra (solid line) of A(1)N (a), A(3)N (b), and A(6)N (c) doped in a PMMA film at 1.0 mol%. Excitation wavelength was 284.0 nm. Applied field strength was 1.0 MV cm^{-1}. E–F spectra (shaded line) and fluorescence spectra (solid line) of A(1)N (d), A(3)N (e), and A(6)N (f) doped in a PMMA film at 5.0 mol%. Excitation wavelength was (d) 281.0 nm, (e) 285.0 nm, and (f) 297.0 nm. Applied field strength was 1.0 MV cm^{-1} for (d and e) and 0.7 MV cm^{-1} for (f). The intensity of the E–F spectrum in (f) is normalized to be in the presence of 1.0 MV cm^{-1} by using its quadratic dependence on applied electric field.

F. Therefore, the present result indicates that the efficiency of the intramolecular EET process is very high both in the absence and in the presence of ***F*** and that the non-radiative process from the fluorescent state remains unchanged in the presence of ***F***. In a stretched PVA film at 10 K, the EET rate constants of A(*n*)N have been determined to be over a hundred times as large as the rate of the fluorescence of 1-methylnaphthalene [14]. Thus, the fluorescence yield of the naphthalene moiety of A(*n*)N should be very low at room temperature, which interferes with the evaluation of the chain length dependence of the field-induced change in EET rate in the present study.

A mixture of anthracene and naphthalene separately doped in a film exhibits different electric field effects on fluorescence. Fig. 4a and b shows the E–F spectra of 1.0 mol% anthracene and of a mixture of 1.0 mol% anthracene and 1.0 mol% naphthalene doped in a PMMA film, respectively, together with their fluorescence spectra. Excitation was done at 343.3 and 287.0 nm, respectively, where the field-induced change in absorption intensity is negligible. As shown in Fig. 4b, only the fluorescence of anthracene is observed in the mixture in spite of the excitation wavelength where the absorption cross-section of naphthalene is 20 times larger than that of anthracene. This indicates that

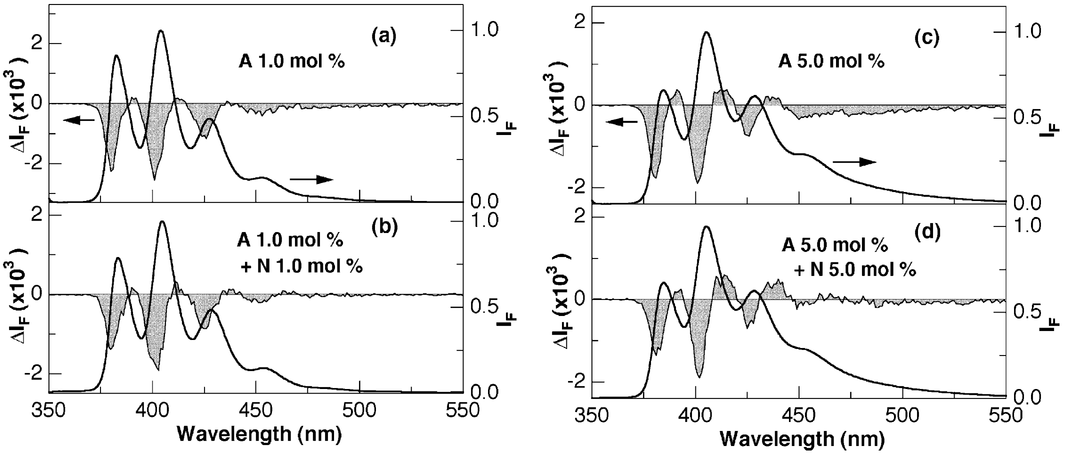

Fig. 4. E–F spectra (shaded line) and fluorescence spectra (solid line) of anthracene (1.0 mol%) (a), a mixture of anthracene (1.0 mol%) and naphthalene (1.0 mol%) (b), anthracene (5.0 mol%) (c), and a mixture of anthracene (5.0 mol%) and naphthalene (5.0 mol%) (d) doped in a PMMA film. Excitation wavelength was 343.3 nm (a), 287.0 nm (b), 343.7 nm (c), and 288.0 nm (d). Applied field strength was 0.7 MV cm^{-1} for (a, c, and d) and 0.8 MV cm^{-1} for (b).

the intermolecular EET process is very efficient even in a mixture separately doped in a PMMA film at 1.0 mol%. It is also seen in Fig. 4a and b that the fluorescence is quenched by ***F***, besides the Stark shift given by a small component of the first derivative of the fluorescence spectrum. The presence of naphthalene does not affect the E–F spectrum of anthracene, although the very efficient intermolecular EET process occurs in a mixture. The fluorescence yield of anthracene is determined by the radiative rate constant that is proportional to the square of the transition moment between the S_1 and S_0 states and the nonradiative rate constant from the S_1 state. Since the transition moment to the S_1 state of anthracene remains unchanged in the presence of ***F***, it can be concluded that the field-induced quenching of the fluorescence both for anthracene and for a mixture of anthracene and naphthalene originates from the field-induced increase in the rate of non-radiative processes from the S_1 state of anthracene. In A(*n*)N, on the other hand, no fluorescence quenching is observed in the E–F spectra observed at a low concentration of 1.0 mol% (see Fig. 3a–c). Thus, the presence of the methylene chain induces a drastic change in electric field effect on the non-radiative decay rate at the S_1 state. A higher triplet state is known to be located near the S_1 state of anthracence [17]. The energy separation between this triplet state and the S_1 state may be shifted by ***F*** because of the difference in molecular polarizability of both states. Such a small change in energy gap may be enough to induce a significant change in the intersystem crossing from the S_1 state to the higher triplet state because both states are accidentally degenerate to each other. By adding a methylene chain, the S_1 state of anthracene chromophore shifts by as much as about 750 cm^{-1} (cf. Figs. 1 and 2 or Figs. 3 and 4), which may result in the negligible electric field effect on intersystem crossing in the linked compounds because of the reduction of the degeneracy between the S_1 state and the higher triplet state.

At a high concentration of A(*n*)N in a PMMA film, the broad fluorescence appears in the longer wavelength region of 425–550 nm, as shown in Fig. 3d–f. Since the excimer of naphthalene is known to exhibit its fluorescence in the 340–450 nm region [18], the observed broad fluorescence can be attributed to the excimer of anthracene or the intermolecular exciplex of anthracene and naphthalene; both fluorescence spectra are expected in this wavelength region [10,19,20]. To clarify the origin of the broad fluorescence of A(*n*)N, we have measured the fluorescence spectra of anthracene and of a mixture of anthracene and naphthalene at different concentrations. Fig. 5a shows the concentration dependence of the fluorescence spectrum of anthracene in a PMMA film. Although the effect of re-absorption is significant in the shorter wavelength region, it is clearly observed that the excimer fluorescence of anthracene appears in the 425–500 nm region with increasing concentration. Fig. 5b shows the fluorescence spectrum of anthracene at 1.0 mol% and that of a mixture of anthracene at 1.0 mol% and naphthalene at 10.0 mol% in a PMMA film. The shapes of these two spectra are essentially the same, indicating that the fluorescence of the exciplex is negligible in a PMMA film. These results lead us to a conclusion that the broad fluorescence of A(*n*)N is attributed to the excimer fluorescence of anthracene. It is known that A(3)N in solution exhibits the fluorescence of the intramolecular exciplex, which results in the cyclization of the two chromophores [10]. In the present study, however, intramolecular exciplex as well as intermolecular exciplex formation is negligible, which may be due to the restriction of the molecular geometry in a PMMA film.

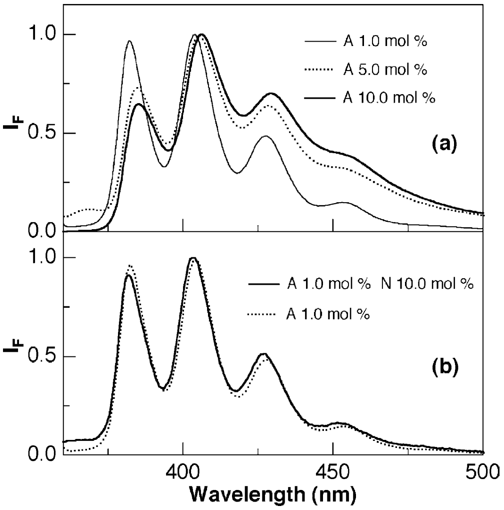

Fig. 5. (a) Fluorescence spectra of anthracene doped in a PMMA film. Fluorescence intensity is normalized to the peak intensity in each spectrum. The concentration was 1.0 mol% (thin-solid line), 5.0 mol% (dotted line), and 10.0 mol% (thick-solid line). (b) Fluorescence spectrum of a mixture of anthracene at 1.0 mol% and naphthalene at 10.0 mol% (solid line) and of anthracene at 1.0 mol% (dotted line) doped in a PMMA film. Excitation wavelength was 277.4 nm for the mixture and 340.6 nm for anthracene.

As shown in Fig. 3d–f, the fluorescence spectra of A(*n*)N at high concentrations show different field-induced changes from those observed at a low concentration of 1.0 mol%. At high concentrations, the fluorescence from the S_1 state of the anthracene chromophore, which is located in the shorter wavelength region, becomes weaker in the presence of ***F***, whereas the excimer fluorescence located in the 425–550 nm region shows the field-induced enhancement. The quenching of the S_1 fluorescence observed at high concentrations can be ascribed to the field-induced acceleration of the rate of the intermolecular non-radiative process from the S_1 state. Owing to the increase in fluorescence of the excimer, it can be argued that the intermolecular excimer formation from the S_1 state is enhanced by ***F*** in the linked compounds. Note that the field-induced change in fluorescence intensity of A(*n*)N is negligible at the low concentration where excimer is not produced (see Fig. 3a–c). In contrast with the linked compounds, the E–F spectra of anthracene exhibit the field-induced de-enhancement at any concentrations both for the S_1 fluorescence and for the excimer fluorescence irrespective of the presence of naphthalene, and the magnitude of the field-induced quenching becomes rather smaller with an increase of the concentration of anthracence, as shown in Fig. 4. The observed differences in field-induced change in fluorescence between A(*n*)N and a mixture show that the methylene chain plays a significant role in the intermolecular excimer formation dynamics and its electric field dependence.

In conclusion, we have measured the E–A and E–F spectra of A(*n*)N and of a mixture of anthracene and naphthalene doped in a PMMA film at various concentrations. All the E–A spectra of the $S_1 \leftarrow S_0$ absorption band of anthracene are similar in shape to the first derivative of the corresponding absorption spectrum. This result indicates that the field-induced change in absorption intensity originates from the change in molecular polarizability following excitation to the S_1 state of anthracene. At low concentrations, the field-induced change in total fluorescence intensity of A(*n*)N is negligibly small, indicating that the efficiency of EET is very large irrespective of the presence of $\boldsymbol{F}$. On the other hand, the quenching of the S_1 fluorescence of anthracence chromophore is observed in the mixture and in anthracene alone, which can be ascribed to the field-induced increase of the rate of non-radiative processes from the S_1 state. At high concentrations, the E–F spectra of A(*n*)N exhibit the field-induced de-enhancement of the S_1 fluorescence and the field-induced enhancement of the excimer fluorescence, while both the S_1 fluorescence and the excimer fluorescence are reduced in a mixture by applying electric fields. The methylene chain is found to restrain the field-induced decrease in non-radiative rate of the S_1 state of anthracene at a low concentration and cause the field-induced enhancement of the excimer fluorescence of anthracene at a high concentration.

Acknowledgements

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